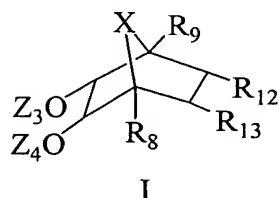


What is claimed:

1. A compound of Formula I:



wherein:

X is CR₁₀R₁₁, O, S or NR₃;

R₃ is C₁-C₁₀ alkyl, substituted C₁-C₁₀ alkyl, -C(=O)alkyl, aryl or an amino protecting group;

each R₁₀ and R₁₁ is, independently, H, C₁-C₁₀ alkyl or substituted C₁-C₁₀ alkyl;

each R₁₂ and R₁₃ is, independently, H, C₁-C₁₀ alkyl, substituted C₁-C₁₀ alkyl, -C(=O)-R₄ or -C(=S)-R₄;

R₄ is -O-C₁-C₁₀ alkyl, -O-C₁-C₁₀ substituted alkyl, -O-aryl or -N(J₁)J₂;

J₁ is H or alkyl;

J₂ is alkyl or a nitrogen protecting group;

or J₁ and J₂ together with the nitrogen atom to which they are attached form a ring structure;

each R₈ and R₉ is, independently, H, C₁-C₁₀ alkyl or substituted C₁-C₁₀ alkyl;

each alkyl substituent is, independently, protected hydroxyl, alkoxy, benzyl, nitro, thioalkyl, aryl, thioaryl, thio substituted aryl, thioalkoxy, or halo;

one of Z₃ and Z₄ is a H or a hydroxyl protecting group and the other of Z₃ and Z₄ is a hydroxyl protecting group or -(L)_n-sm wherein when both Z₃ and Z₄ are hydroxyl protecting groups said protecting groups are orthogonal to each other; and

L is a linking moiety;

n is 0 or 1; and

sm is a support medium.

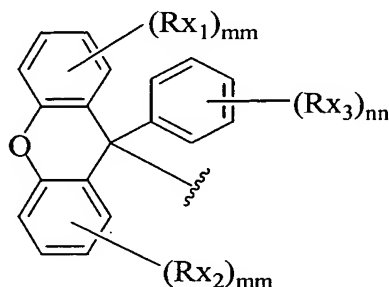
2. The compound of claim 1 wherein X is O, CH₂, S or NR₃;

3. The compound of claim 2 wherein X is O or CH₂.

4. The compound of claim 1 wherein X is O, one of Z₃ and Z₄ is -(L)_n-sm and the other of Z₃ and Z₄ is a hydroxyl protecting group or H.
5. The compound of claim 1 wherein X is NR₃ and R₃ is alkyl or -C(=O)alkyl.
6. The compound of claim 1 wherein R₈ and R₉ are both H.
7. The compound of claim 6 wherein L is succinyl, oxalyl, -C(=O)- or -C(=O)-NH-.
8. The compound of claim 1 wherein one of R₁₂ and R₁₃ is H and the other of R₁₂ and R₁₃ is C₁-C₁₀ alkyl or substituted C₁-C₁₀ alkyl.
9. The compound of claim 1 wherein R₁₂ and R₁₃ are each H.
10. The compound of claim 1 wherein one of Z₃ and Z₄ is -(L)_n-sm and the other of Z₃ and Z₄ is a hydroxyl protecting group.
11. The compound of claim 10 wherein said L is a succinyl or an oxalyl group.
12. The compound of claim 10 wherein said hydroxyl protecting group is dimethoxytrityl.
13. The compound of claim 1 wherein one of Z₃ and Z₄ is trimethylsilyl, triethylsilyl, *t*-butyldimethylsilyl, *t*-butyldiphenylsilyl, triphenylsilyl, benzoylformyl, acetyl, chloroacetyl, dichloroacetyl, trichloroacetyl, trifluoroacetyl, pivaloyl, benzoyl, *p*-phenylbenzoyl, 9-fluorenylmethoxycarbonyl, levulinyl or an acetoacetyl group and the other of Z₃ and Z₄ is 4,4'-dimethoxytrityl, monomethoxytrityl, 9-phenylxanthen-9-yl, 9-(*p*-methoxyphenyl)xanthen-9-yl, *t*-butyl, *t*-butoxymethyl, methoxymethyl, tetrahydropyranyl, 1-ethoxyethyl, 1-(2-chloroethoxy)ethyl, 2-trimethylsilylethyl, *p*-chlorophenyl, 2,4-dinitrophenyl, benzyl, 2,6-dichlorobenzyl, diphenylmethyl, *p,p*-dinitrobenzhydryl, *p*-nitrobenzyl, triphenylmethyl, trimethylsilyl, triethylsilyl, *t*-butyldimethylsilyl, *t*-butyldiphenylsilyl, triphenylsilyl, benzoylformate, acetyl, chloroacetyl, trichloroacetyl, trifluoroacetyl, pivaloyl, benzoyl, *p*-phenylbenzoyl, mesyl, tosyl, 4,4',4''-tris-

(benzyloxy)trityl, 4,4',4''-tris-(4,5-dichlorophthalimido)trityl, 4,4',4''-tris(levulinyloxy)trityl, 3-(imidazolymethyl)-4,4'-dimethoxytrityl, 4-decyloxytrityl, 4-hexadecyloxytrityl, 9-(4-octadecyloxyphenyl)xanthene-9-yl, 1,1-bis-(4-methoxyphenyl)-1'-pyrenyl methyl, p-phenylazophenyloxycarbonyl, 9-fluorenylmethoxycarbonyl, 2,4-dinitrophenylethoxycarbonyl, 4-(methylthiomethoxy)butyryl, 2-(methylthiomethoxymethyl)-benzoyl, 2-(isopropylthiomethoxymethyl)benzoyl, 2-(2,4-dinitrobenzenesulphenyloxymethyl)benzoyl, or a levulinyl group.

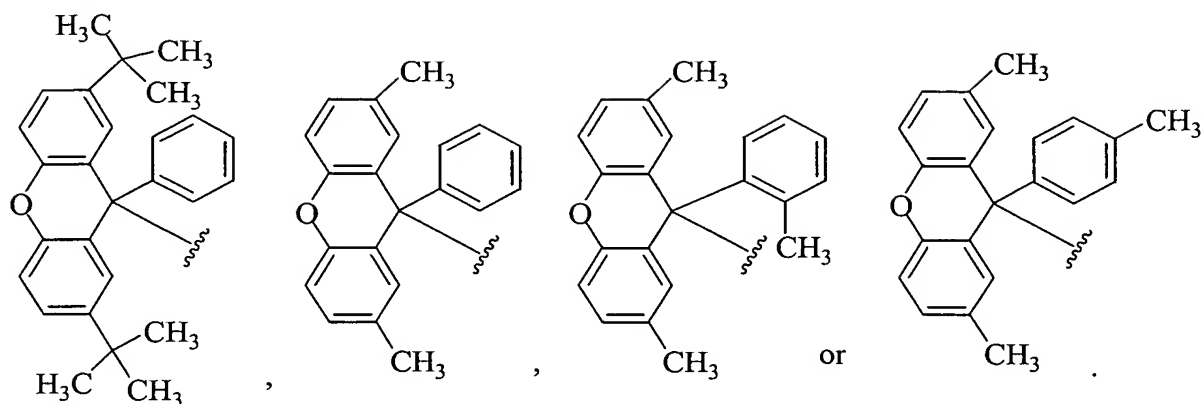
14. The compound of claim 1 wherein one of Z_3 and Z_4 has the formula:



wherein

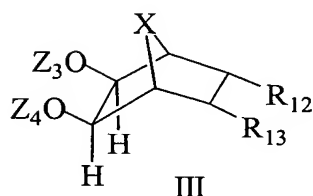
each Rx_1 is, independently, C_1 - C_{10} alkyl or branched C_1 - C_{10} alkyl;
 each Rx_2 is, independently, C_1 - C_{10} alkyl or branched C_1 - C_{10} alkyl;
 each Rx_3 is, independently, C_1 - C_{10} alkyl or branched C_1 - C_{10} alkyl;
 each mm is, independently, 0, 1, 2 or 3; and
 nn is 0, 1, 2 or 3.

15. The compound of claim 14 wherein nn is 0.
16. The compound of claim 14 wherein nn is 1 and Rx_3 is C_1 - C_{10} alkyl.
17. The compound of claim 14 wherein nn is 1 and Rx_3 is a methyl group in the para or ortho position of the phenyl ring.
18. The compound of claim 14 wherein the other of Z_3 and Z_4 is H.
19. The compound of claim 14 wherein one of Z_3 and Z_4 has one of the formulas:



20. The compound of claim 19 wherein the other of Z_3 and Z_4 is H.

21. The compound of claim 1 having formula III:



wherein:

X is O or CH_2 ;

each R_{12} and R_{13} is, independently, H, C_1 - C_{10} alkyl, substituted C_1 - C_{10} alkyl, $-C(=O)-R_4$ or $-C(=S)-R_4$;

R_4 is $-O-C_1-C_{10}$ alkyl, $-O-C_1-C_{10}$ substituted alkyl, $-O$ -aryl or $-N(J_1)J_2$;

J_1 is H or alkyl;

J_2 is alkyl or a nitrogen protecting group;

or J_1 and J_2 together with the nitrogen atom to which they are attached form a ring structure;

one of Z_3 and Z_4 is a H or a hydroxyl protecting group and the other of Z_3 and Z_4 is a hydroxyl protecting group or $-(L)_n$ -sm wherein when both Z_3 and Z_4 are hydroxyl protecting groups said protecting groups are orthogonal to each other;

L is a linking moiety;

n is 0 or 1; and

sm is a support medium.

22. The compound of claim 21 wherein one of Z_3 and Z_4 is $-(L)_n$ -sm and the other of Z_3 and Z_4 a hydroxyl protecting group or H.

23. The compound of claim 22 wherein said L is a succinyl or an oxalyl group.

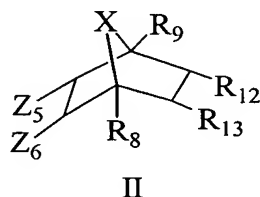
24. The compound of claim 22 wherein the other of Z_3 and Z_4 is dimethoxytrityl.

25. The compound of claim 21 wherein said support medium is a controlled pore glass, oxalyl-controlled pore glass, silica-containing particles, polymers of polystyrene, copolymers of polystyrene, copolymers of styrene and divinylbenzene, copolymers of dimethylacrylamide and N,N'-bisacryloylthylenediamine, soluble support medium, or PEPS.

26. The compound of claim 25, wherein said support medium is controlled pore glass, polymers of polystyrene or copolymers of polystyrene.

27. A method for functionalizing a support medium with a first monomeric subunit, comprising:

providing a support bound compound of Formula II:



wherein:

X is $CR_{10}R_{11}$, O, S or NR_3 ;

R_3 is C_1 - C_{10} alkyl, substituted C_1 - C_{10} alkyl, $-C(=O)$ alkyl, aryl or an amino protecting group;

each R_{10} and R_{11} is, independently, H, C_1 - C_{10} alkyl or substituted C_1 - C_{10} alkyl;

each R_{12} and R_{13} is, independently, H, C_1 - C_{10} alkyl, substituted C_1 - C_{10} alkyl, $-C(=O)-R_4$ or $-C(=S)-R_4$;

R_4 is $-O-C_1-C_{10}$ alkyl, $-O-C_1-C_{10}$ substituted alkyl, $-O$ -aryl or $-N(J_1)J_2$;

J_1 is H or alkyl;

J_2 is alkyl or a nitrogen protecting group;

or J_1 and J_2 together with the nitrogen atom to which they are attached form a ring structure;

each R_8 and R_9 is, independently, H, C_1-C_{10} alkyl or substituted C_1-C_{10} alkyl;

each alkyl substituent is, independently, protected hydroxyl, alkoxy, benzyl, nitro, thioalkyl, aryl, thioaryl, thio substituted aryl, thioalkoxy, or halo;

one of Z_5 and Z_6 is a protected hydroxyl group and the other of Z_5 and Z_6 is $-O-(L)_n$ -sm;

L is a linking moiety;

n is 0 or 1; and

sm is a support medium;

deprotecting said protected hydroxyl group to give a reactive hydroxyl group; and treating said reactive hydroxyl group with a first monomeric subunit having an activated phosphorus group and a further protected hydroxyl group thereon for a time and under conditions sufficient to form a monomer-functionalized support medium.

28. The method of claim 27, further comprising:

treating said monomer-functionalized support medium with a capping agent;

and

optionally, treating said monomer-functionalized support medium with an oxidizing agent.

29. The method of claim 28, further comprising:

deblocking said further protected hydroxyl group to give a reactive hydroxyl group;

treating said reactive hydroxyl group with a further monomeric subunit having an activated phosphorus group and a further protected hydroxyl group thereon for a time and under conditions sufficient to form an extended compound;

treating said extended compound with a capping agent;

optionally, treating said extended compound with an oxidizing or sulfurizing agent;

repeating the preceding four steps one or more times to form a further extended compound; and

treating said further extended compound with an oxidizing or sulfurizing agent to form an oligomeric compound.

30. The method of claim 29, wherein treating said further extended compound with said oxidizing agent to form said oligomeric compound removes protecting groups present on said oligomeric compound.

31. The method of claim 29, further comprising a step of treating said oligomeric compound with a reagent effective to cleave said oligomeric compound from said support medium.

32. The method of claim 31, wherein said reagent is a solution of ammonia.

33. The method of claim 31, wherein said cleaved oligomeric compound has a terminal hydroxyl group at the site of cleavage.

34. The method of claim 33, wherein said terminal hydroxyl group is attached to the 2'- or 3'-position of the nucleoside that is located at the 3'-terminus of said oligomeric compound.

35. The method of claim 34, wherein said terminal hydroxyl group is attached to the 2'-position of the nucleoside that is located at the 3'-terminus of said oligomeric compound.

36. The method of claim 29, wherein said treating of said reactive hydroxyl group with a further monomeric subunit is performed in the presence of an activating agent.

37. The method of claim 27, wherein X is O, S or NR₃.

38. The method of claim 27, wherein R₃ is alkyl or -C(=O)alkyl.

39. The compound of claim 27 wherein n is 1.

40. The method of claim 39, wherein L is succinyl, oxalyl, -C(=O)- or -C(=O)-NH-.

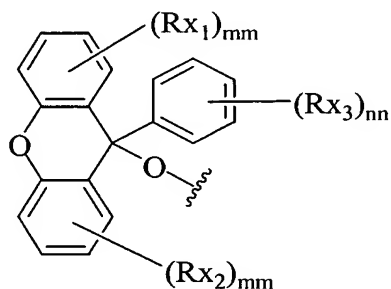
41. The method of claim 27, wherein said support medium is controlled pore glass, oxalyl-controlled pore glass, silica-containing particles, polymers of polystyrene, copolymers of polystyrene, copolymers of styrene and divinylbenzene, copolymers of dimethylacrylamide and N,N'-bisacryloylethylenediamine, soluble support medium or PEPS.

42. The method of claim 41, wherein said support medium is controlled pore glass, polymers of polystyrene or copolymers of polystyrene.

43. The method of claim 27, wherein one of Z₃ and Z₄ is trimethylsilyl, triethylsilyl, *t*-butyldimethylsilyl, *t*-butyldiphenylsilyl, triphenylsilyl, benzoylformyl, acetyl, chloroacetyl, dichloroacetyl, trichloroacetyl, trifluoroacetyl, pivaloyl, benzoyl, *p*-phenylbenzoyl, 9-fluorenylmethoxycarbonyl, levulinyl or acetoacetyl and the other of Z₃ and Z₄ is 4,4'-dimethoxytrityl, monomethoxytrityl, 9-phenylxanthen-9-yl, 9-(*p*-methoxyphenyl) xanthen-9-yl, *t*-butyl, *t*-butoxymethyl, methoxymethyl, tetrahydropyranyl, 1-ethoxyethyl, 1-(2-chloroethoxy)ethyl, 2-trimethylsilylethyl, *p*-chlorophenyl, 2,4-dinitrophenyl, benzyl, 2,6-dichlorobenzyl, diphenylmethyl, *p,p*-dinitrobenzhydryl, *p*-nitrobenzyl, triphenylmethyl, trimethylsilyl, triethylsilyl, *t*-butyldimethylsilyl, *t*-butyldiphenylsilyl, triphenylsilyl, benzoylformate, acetyl, chloroacetyl, trichloroacetyl, trifluoroacetyl, pivaloyl, benzoyl, *p*-phenylbenzoyl, mesyl, tosyl, 4,4',4''-tris-(benzyloxy)trityl, 4,4',4''-tris-(4,5-dichlorophthalimido)trityl, 4,4',4''-tris(levulinylloxy)trityl, 3-(imidazolylmethyl)-4,4'-dimethoxytrityl, 4-decyloxytrityl, 4-hexadecyloxytrityl, 9-(4-octadecyloxyphenyl)xanthene-9-yl, 1,1-bis-(4-methoxyphenyl)-1'-pyrenyl methyl, *p*-phenylazophenylloxycarbonyl, 9-fluorenylmethoxycarbonyl, 2,4-dinitrophenylethoxy carbonyl, 4-(methylthiomethoxy)butyryl, 2-(methylthiomethoxymethyl)-benzoyl, 2-(isopropylthiomethoxymethyl)benzoyl, 2-(2,4-dinitrobenzenesulphenyloxymethyl)benzoyl, or a levulinyl group.

44. The method of claim 27, wherein said monomeric subunit having an activated phosphorus group is a phosphoramidite, an H-phosphonate or a phosphate triester.

45. The method of claim 44, wherein said monomeric subunit is a phosphoramidite.
46. The method of claim 27, wherein Z_5 is an acid labile hydroxyl-protecting group.
47. The method of claim 29, wherein each of said further hydroxyl protecting groups is acid labile.
48. The method of claim 47, wherein said further hydroxyl protecting groups are removed by contact with an acid, wherein said acid is formic acid, acetic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid, trifluoroacetic acid, benzenesulfonic acid, toluenesulfonic acid, or phenylphosphoric acid.
49. The method of claim 29, wherein said oligomeric compound is an oligonucleotide, modified oligonucleotide, oligonucleotide analog, oligonucleoside, oligonucleotide mimetic, hemimer, gapmer or chimera.
50. The method of claim 49, wherein said oligomeric compound is an oligonucleotide.
51. The method of claim 27, wherein one of Z_5 and Z_6 has the formula:



wherein

- each Rx_1 is, independently, C_1 - C_{10} alkyl or branched C_1 - C_{10} alkyl;
- each Rx_2 is, independently, C_1 - C_{10} alkyl or branched C_1 - C_{10} alkyl;
- each Rx_3 is, independently, C_1 - C_{10} alkyl or branched C_1 - C_{10} alkyl;
- each mm is, independently, 0, 1, 2 or 3; and

nn is 0, 1, 2 or 3.

52. The method of claim 51 wherein nn is 0.

53. The method of claim 51 wherein nn is 1 and Rx_3 is C_1 - C_{10} alkyl.

54. The method of claim 53 wherein Rx_3 is a methyl group in the para or ortho position of the phenyl ring.